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Influence of convective transport on tropospheric ozone and its precursors in a chemistry-climate model

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Abstract. The impact of convection on tropospheric O₃ and its precursors has been examined in a coupled chemistry-climate model. There are two ways that convection affects O₃. First, convection affects O₃ by vertical mixing of O₃ itself. Convection lifts lower tropospheric air to regions where the O₃ lifetime is longer, whilst mass-balance subsidence mixes O₃-rich upper tropospheric (UT) air downwards to regions where the O₃ lifetime is shorter. This tends to decrease UT O₃ and the overall tropospheric column of O₃. Secondly, convection affects O₃ by vertical mixing of O₃ precursors. This affects O₃ chemical production and destruction. Convection transports isoprene and its degradation products to the UT where they interact with lightning NO_x to produce PAN, at the expense of NO_x. In our model, we find that convection reduces UT NO_x through this mechanism; convective down-mixing also flattens our imposed profile of lightning emissions, further reducing UT NO_x. Over tropical land, which has large lightning NO_x emissions in the UT, we find convective lofting of NO_x from surface sources appears relatively unimportant. Despite UT NO_x decreases, UT O₃ production increases as a result of UT HO_x increases driven by isoprene oxidation chemistry. However, UT O₃ tends to decrease, as the effect of convective overturning of O₃ itself dominates over changes in O₃ chemistry. Convective transport also reduces UT O₃ in the mid-latitudes resulting in a 13% decrease in the global tropospheric O₃ burden. These results contrast with an earlier study that uses a model of similar chemical complexity. Differences in convection schemes as well as chemistry schemes – in particular isoprene-driven changes are the most likely causes of such discrepancies. Further modelling studies are needed to constrain this uncertainty range.

1 Introduction

The parameterisation of sub-grid scale convection is known to be a major uncertainty in both chemistry transport models (CTMs) and general circulation models (GCMs). A substantial element of divergence amongst CTM simulations arises from differences in convection parameterisation schemes, which have a particularly large influence on the distributions of short-lived species such as NO_x (NO+NO₂), HO_x (OH+HO₂), and ozone (O₃) (Prather and Jacob, 1997; Collins et al., 1999; Prather et al., 2001; Gauss et al., 2003; Lawrence and Rasch, 2005). Future emissions projections (e.g., Nakicenovic et al., 2000) indicate strong growth of O₃ precursor emissions in the tropics – how these are processed by convection will be an important determinant of future O₃ concentrations and the oxidising capacity of the atmosphere. GCM simulations project future regional changes in the distribution of convection over many parts of the globe (Cubasch et al., 2001). On interannual timescales shifts in convection associated with the El Niño Southern Oscillation modulate tropical tropospheric chemistry variability (Ziemke and Chandra, 2003). Convection is therefore important in the context of understanding how climate variability and future climate change may affect tropospheric chemistry, via changes in both vertical mixing and the distribution of lightning NO_x (e.g., Stevenson et al., 2005a).

Since O₃, its lifetime and its production efficiency per NO_x molecule all typically increase with height, deep convection strongly affects O₃ and its precursors throughout the tropical tropospheric column (TTC), as shown in numerous measurement and modelling studies (e.g. Dickerson et al., 1987; Pickering et al., 1990, 1995). Considering O₃ in isolation, increased vertical mixing tends to lower TTC O₃, as O₃-poor air mixes upwards, to regions where its lifetime is longer, whilst O₃-rich air mixes downwards through mass-balance subsidence, to regions where its lifetime is shorter (e.g., Lelieveld and Crutzen, 1994; Lawrence et al., 2003).

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However, the effects of convection on O_3 precursors also need to be considered. Where there are surface O_3 precursor sources, especially short-lived ones such as NO_x , isoprene (C_5H_8) and other natural or anthropogenic hydrocarbons, convection significantly increases these precursor concentrations in the mid- and upper-troposphere (MT and UT) at the expense of lower troposphere (LT). Collins et al. (1999) and von Kuhlmann et al. (2004) identify convective uplifting of isoprene and its degradation products as a major source of tropical UT HO_x . Lawrence et al. (2003) find that lofting of surface NO_x is a significant driver of increases in O_3 production over much of the tropospheric column. Lightning in the tropics is a major NO_x source directly associated with convection, with most NO_x added to the UT (Pickering et al., 1998). There are also potential interactions between isoprene and lightning emissions (e.g., von Kuhlmann et al., 2004). An important isoprene degradation product is the peroxy acetyl radical (CH_3COO_2), which can affect NO_x by promoting PAN formation over land areas where isoprene and lightning NO_x emissions are co-located. The net impact of convective mixing is thus sensitive to the profile of O_3 and its precursors prior to convection, and is a complex balance between transport and a variety of chemical effects. Lawrence et al. (2003) found the effect of convective changes in precursor emissions on the tropospheric O_3 burden to be more important than the convective redistribution of O_3 .

In this paper, the role of convective mixing in determining the distribution of O_3 and its precursors is investigated using the STOCHEM-HadAM3 coupled chemistry-climate model. Section 2 describes the model and the experiments. Section 3 describes the distribution of convection and evaluates model results with observations. Then the influence of convection on O_3 , its precursors and on O_3 production and destruction is discussed for tropical land and ocean. Changes to the global O_3 budget related to convection are then outlined. Section 4 discusses the results of this paper compared to those from other studies, highlights model differences and uncertainties; Sect. 5 presents conclusions.

2 Model and experiments

The current version of STOCHEM-HadAM3 coupled CTM-GCM model has been described in detail in previous studies (Sanderson et al., 2003a, b; Stevenson et al., 2004), so we present a limited description of relevant model processes here. HadAM3 (Pope et al., 2000) is the atmospheric component of the HadCM3 atmosphere-ocean general circulation model (GCM). HadAM3 was driven by prescribed monthly sea-surface temperatures (SSTs) for 1980–2002 and was run at standard resolution of 3.75° longitude by 2.5° latitude and 19 vertical levels. These levels are concentrated at the surface and extend to 10 hPa. Meteorological fields are passed to the CTM every 3 h.

STOCHEM is a Lagrangian tropospheric CTM, first described by Collins et al. (1997), with subsequent major updates to the chemistry (Collins et al., 1999), convection (Collins et al., 2002) and deposition schemes (Sanderson et al., 2003a). Its atmosphere is divided into 50 000 equal mass air parcels that are advected by HadAM3 winds. Air parcels are mapped onto a 5° longitude by 5° latitude horizontal grid with 9 equally spaced vertical levels, which extends from the surface to ~ 100 hPa. Stratospheric O_3 influx, calculated from a present-day stratospheric O_3 climatology (Li and Shine, 1995), is distributed into the troposphere by HadAM3 vertical winds at 100 hPa as a flux term. This means that the stratospheric influx should not be affected by convective mixing, since neither the 100 hPa winds or O_3 climatology are changed; the small change in inferred O_3 stratospheric influx (calculated as a residual term) in Table 1 (Sect. 3.4) reflects random differences in air parcel sampling of the atmosphere between model simulations. Stratospheric input of HNO_3 is modelled similarly assuming a fixed N: O_3 ratio of 1:1000 (Murphy and Fahey, 1994). In this study, the chemical fields from STOCHEM are not fed back into the radiation scheme in HadAM3.

The convection scheme in HadAM3 is a bulk mass-flux scheme with an instability closure (Gregory et al., 1997) and is based on that of Tiedtke (1989). STOCHEM uses the Collins et al. (2002) Lagrangian convective mixing scheme. This mixing scheme uses the 3-D convective updraught mass fluxes generated from HadAM3 and represents rapid convective updraughts, entrainment and detrainment of air parcels, and slower mass balance subsidence of larger regions of surrounding air. Although downdraughts are calculated in the GCM convection scheme, these are not implemented in the mixing scheme. Collins et al. (2002) compare simulated radon (^{222}Rn) profiles against available measurements. These were summertime mid-latitude continental and coastal sites. The Lagrangian mixing scheme compares favourably with observations in the continental regions. In coastal regions, the model underestimates radon in the boundary layer but elsewhere shows good agreement. Tropical surface simulations of ^{222}Rn were also evaluated, and similar results to those of earlier modelling studies were found – with ^{222}Rn underestimates in spring at Mauna Loa, and ^{222}Rn overestimates/underestimates in spring/summer at Bermuda. Further details can be found in Collins et al. (2002).

Generation of lightning NO_x is linked to the convection scheme following Price et al. (1997). Convective precipitation from HadAM3 is used to identify lightning occurrence, and cloud height and thickness used to calculate the number of flashes for marine and continental clouds. The global production of lightning NO is scaled to be roughly 7 Tg N/yr and global isoprene emissions are $\sim 575\text{ Tg yr}^{-1}$. The profiles of Pickering et al. (1998) are used to vertically distribute the lightning NO_x emissions for three regimes: mid-latitude continental, tropical continental and tropical marine; mid-latitude marine regions are treated like tropical

marine regions. For these three regimes most lightning NO_x (55–75% depending on regime) is emitted in the UT above 8 km. The modelled global annual-average lightning NO_x spatial distribution is in fairly good agreement with the lightning flash rate recently derived from satellite by Christian et al. (2003). Note that only a qualitative comparison is possible since NO emissions are not directly proportional to the total number of flashes, as the cloud-to-ground and inter-cloud flashes produce different amounts of NO_x . However, the global annual land to ocean ratio of lightning NO_x emissions in our model is $\sim 30:1$, whilst the land/ocean lightning flash rate derived by Christian et al. (2003) is 10:1. Since modelled and observed precipitation climatologies have high spatial agreement (not shown), this suggests that oceanic lightning NO_x is underestimated by the Price et al. (1997) scheme. This was also found by Labrador et al. (2005). In our model set-up we use the Pickering et al. (1998) vertical profiles to distribute lightning NO_x emissions in all simulations (even when convective mixing is switched off). Consequently, in the control experiment these distributed emissions are then also subject to convective mixing once they enter the model transport and mixing schemes.

Two experiments were performed for the period 1980–2000: a “control” experiment with normal convective mixing of O_3 and its precursors, and a “convection off” experiment with no convective mixing of O_3 or its precursors, although convection in the climate model and lightning NO_x emissions (see above) still occur. Water vapour concentrations also do not change between the two experiments.

Anthropogenic and natural emissions of global trace gases in both experiments are identical. Anthropogenic emissions come from the SRES A2 scenario (Nakićenović et al., 2000) for the present-day period. Note that emissions from all the different SRES scenarios are similar over this period. Natural emissions are as given in Stevenson et al. (2004). For analysis, two different tropopause definitions were used: (i) a chemical tropopause defined using the 150 ppbv O_3 isopleth (the definition used by Prather et al. (2001); and (ii) a physical tropopause based on the WMO definition and diagnosed in HadAM3. In both cases the same tropopause mask was used for the analysis of the control and convection off simulations. For the chemical tropopause this involved masking any grid boxes where monthly-mean O_3 mixing ratios exceeded 150 ppbv in either of the two simulations.

3 Results

Figure 1a depicts annual-average convective updraught mass fluxes from HadAM3 for 1991–1996 (to be coincident with the ERA-40 reanalyses period, see below). Deep convection in the inter-tropical convergence zone (ITCZ) and South Pacific Convergence Zone is clearly delineated (Figs. 1a, b). Substantial convection at ~ 200 hPa ($\text{eta}=0.2$) can also be seen over SE Asia, southern N America, and E Siberia/Japan

(Fig. 1a). Convection that extends up to the MT is also depicted in the tropics and in mid-latitudes, particularly over the southern oceans and northern continents, and is typically associated with frontal activity (Fig. 1b). The anomalies over the Himalayas are non-precipitating convection and appear to be a consequence of model orography. Convective updraught mass fluxes from ERA-40 reanalyses (“on-line” fluxes – see Sect. 4; Oliv   et al., 2004) are displayed in Figs. 1d–f. Compared to ERA-40, HadAM3 has higher mass fluxes (by up to a factor of 2) and convection also generally reaches greater altitudes (Figs. 1c, f). It should be stressed that the distribution and strength of convection are poorly constrained by observations, and it is not obvious that ERA-40 values reflect the real atmosphere, although they perhaps represent our best current estimate.

3.1 Evaluation of modelled NO_x , PAN and O_3 against observations

Several aircraft campaigns have measured atmospheric composition, and these provide useful data to evaluate model simulations. Emmons et al. (2000) produced data composites for several species, including NO_x , PAN and O_3 – these have been updated to incorporate subsequent campaigns, and the data have been binned onto a $5^\circ \times 5^\circ \times 1$ km grid (see <http://gctm.acd.ucar.edu/data>). Figure 2 plots annual mean profiles for the tropics over land and ocean. Each point in the vertical profile represents the mean of several grid boxes – in turn these represent the mean of several aircraft measurements. The numbers adjacent to the right-hand vertical axis indicate the number of grid boxes contributing to the mean. In addition, the standard deviation of the grid boxes is depicted by a box surrounding the mean value. It should be noted that these observed profiles sample only a small fraction of the atmosphere, both spatially and temporally. Also plotted in Fig. 2 are model results, sampled in the same way as the mean observations for the control (solid red line) and convection off simulations (solid green line). The ± 1 standard deviation for the control simulation is also depicted (red dashed line). Annual-mean profiles for the mid-latitudes can be seen at http://www.met.ed.ac.uk/~dstevens/convection_paper/midlatseval.pdf.

Figures 2a and d are for NO_x , and show a “C”-shaped profile over land. Over tropical land, the model somewhat underestimates NO_x in the LT, and overestimates NO_x in the UT. This may be due to over-vigorous convection, or perhaps deficiencies in either the lightning NO_x emission profiles and/or our application of these in STOCHEM as discussed in Sect. 2. In a parallel study, with perturbed lightning NO_x emissions, we found that a reduction in global lightning NO production from 7 to 3.5 Tg N/yr led to an underestimate of tropical UT NO_x , and a larger underestimate of mid-latitude MT NO_x (see below). Over the oceans, the LT is better represented, but here UT NO_x is underestimated. This may reflect an underestimate of lightning over the oceans

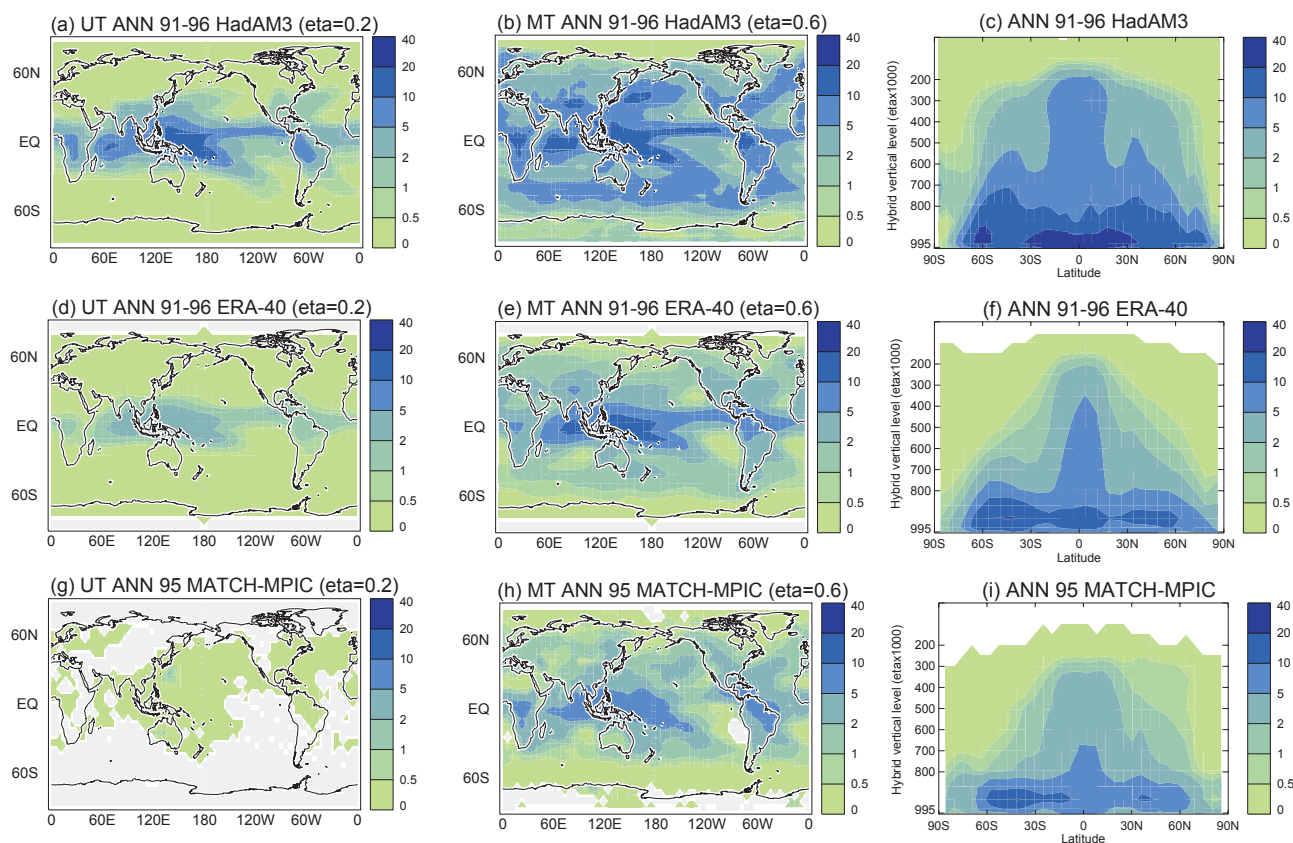


Fig. 1. Annual-average convective updraught mass fluxes ($\text{g/m}^2/\text{s}$) in the UT ($\eta=0.2$, ~ 200 hPa), MT ($\eta=0.6\sim 600$ hPa) and zonal-mean vs. altitude fluxes derived from HadAM3 (1991–1996) (a–c), ERA-40 reanalyses (1991–1996) (d–f) and MATCH-MPIC (1995) (g–i).

compared to the land. As discussed in Sect. 2, the model's interactive lightning scheme generates a land: ocean ratio in lightning NO_x emissions that is rather more land-biased than recent satellite observations suggest. Nevertheless, model and observations are nearly always within a standard deviation of each other. The convection off profile (in green) clearly shows the strong enhancement in tropical UT NO_x that occurs when convective mixing is switched off; this is partially due to the fact that the lightning NO_x profile is still applied in the convection off case, and there is less down-mixing of this major UT NO_x source. In the mid-latitudes UT NO_x is underestimated and LT NO_x overestimated, particularly over land (not shown). This could suggest too little convective mixing in mid-latitudes (although this would be surprising given that HadAM3 convective updraught mass fluxes are stronger than those derived from ERA-40 reanalyses, as discussed in Sect. 3). Underestimates in UT NO_x may also arise because of PAN over-production (see below) or under-estimation of mid-latitude lightning NO_x sources.

Figures 2b and e show PAN profiles, and again show generally good agreement, although with a slight tendency for the model to overestimate PAN, particularly in the UT. This tendency for the model to overestimate PAN is more evident

in northern mid-latitudes (not shown), and may reflect over-production of the peroxy acetyl radical from higher hydrocarbons. The convection off profile for the tropics clearly shows the major influence of convection on PAN in the model, almost doubling its MT and UT concentrations over land, due to the vertical lofting of relatively short-lived hydrocarbons and their degradation products (in particular isoprene-related species). In turn, convection-enhanced PAN formation contributes to the reductions in UT NO_x (Figs. 2a and d).

Finally, Figs. 2c and f show tropical O_3 profiles. The model typically underestimates O_3 throughout the profile, by around 5–10 ppbv over land and 10–15 ppbv over the ocean. A similar underestimate was also found for the same model (but with slightly different emissions) in the O_3 evaluation against ozonesonde data performed in Stevenson et al. (2004) and Dentener et al. (2005). It seems likely that the O_3 destruction chemistry is rather too active in the model – in a recent model inter-comparison (Stevenson et al., 2005b), the STOCHEM model coupled to HadAM3 had the shortest tropospheric O_3 lifetime of all the models sampled. The ozone lifetime is mainly determined by the flux through the main O_3 sink ($\text{O}(^1\text{D})+\text{H}_2\text{O}$). This reaction is also the main source of OH. The model's methane lifetime (and hence tropical

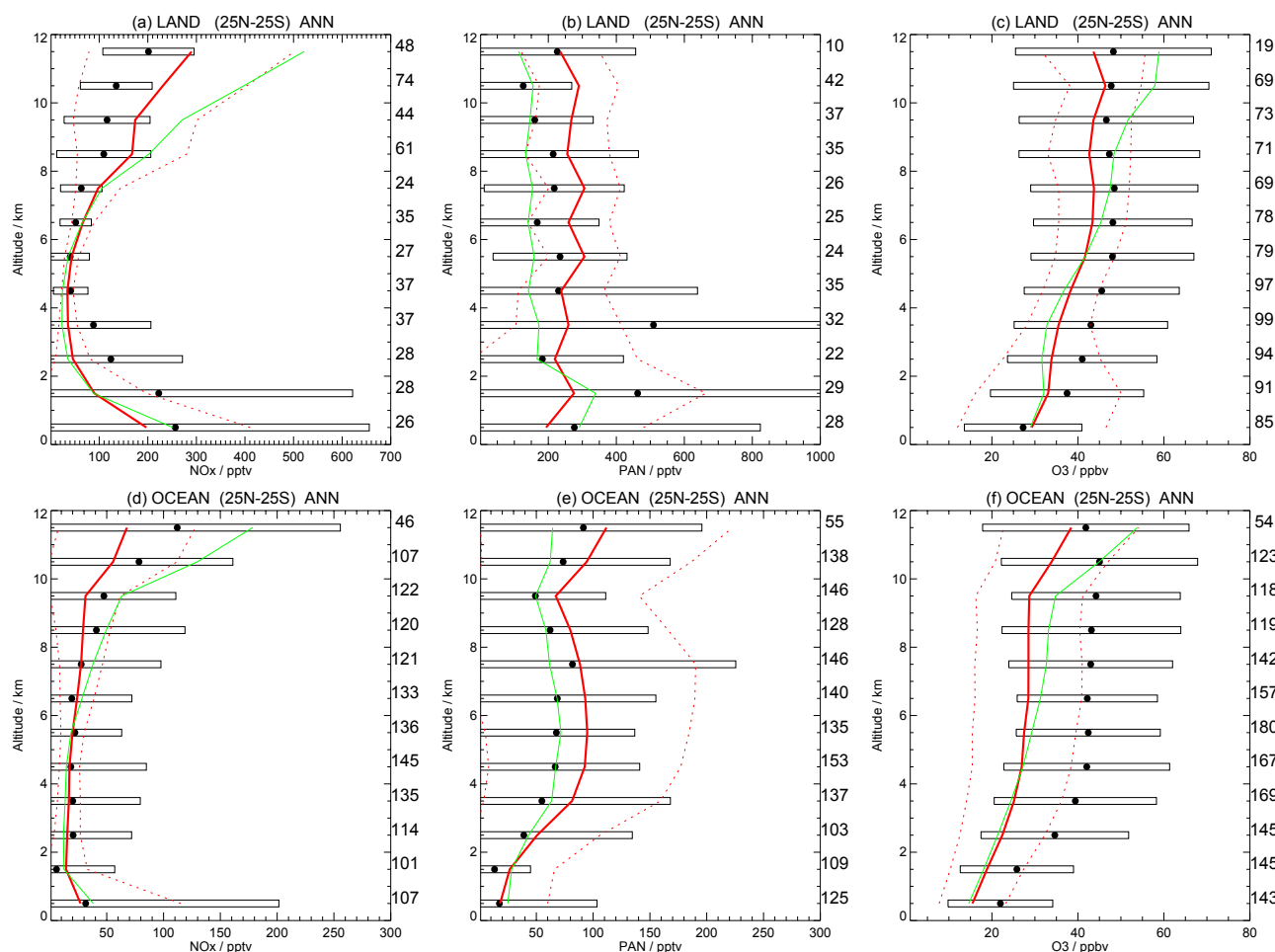


Fig. 2. NO_x (a, b), PAN (c, d) and O_3 (e, f) simulated and observed profiles over tropical land and ocean. The points represent annual mean tropical (25°N – 25°S) profiles and are mean values of gridded aircraft measurements from the SASS database <http://gctm.acd.ucar.edu/data> (Emmons et al., 2000). The numbers adjacent to the right-hand vertical axis indicate the number of grid boxes contributing to the mean. The standard deviation is depicted by a box surrounding the mean value. The curves represent HadAM3-STOCHEM model mean values for the same spatial and temporal locations as the observations for the control (red) and convection off (green) simulations. The standard deviation for the control simulation is denoted by dashed lines.

OH) was found to be near the central estimate of Prather et al. (2001), and close to the model average in the same inter-comparison; this suggests that the OH source term is approximately correct. It may be that the second largest O_3 sink (reaction with HO_2) is overestimated by the model – this may tie in with the potentially over-active hydrocarbon chemistry suggested by the high PAN levels. At this stage, we do not fully understand the low O_3 bias in the tropics. In the mid-latitudes this bias is smaller and is confined to the LT and MT.

These model comparisons against observations indicate the model has some skill in simulating NO_x , PAN and O_3 , but also has some significant biases. Nevertheless, the model is generally within ± 1 standard deviation of observations, and represents a comparable model to others used for similar

studies to assess the influence of convective mixing upon O_3 and its precursors.

3.2 Influence of convection over tropical land and ocean

Figure 3 depicts annual zonal mean tropical O_3 and NO_x concentrations for tropical land and ocean regions separately (Figs. 3a–d) for the control experiment (i.e. normal convective mixing) and the impact of switching on convective mixing (Figs. 3e–h). Many of the features described below can be seen in the model profiles in Fig. 2. For simplicity we discuss Fig. 3 results alone below.

Both species are generally higher over land, where the main NO_x surface and UT lightning sources are located. The O_3 lifetime and production efficiency increase with height – these factors, in conjunction with the stratospheric source of

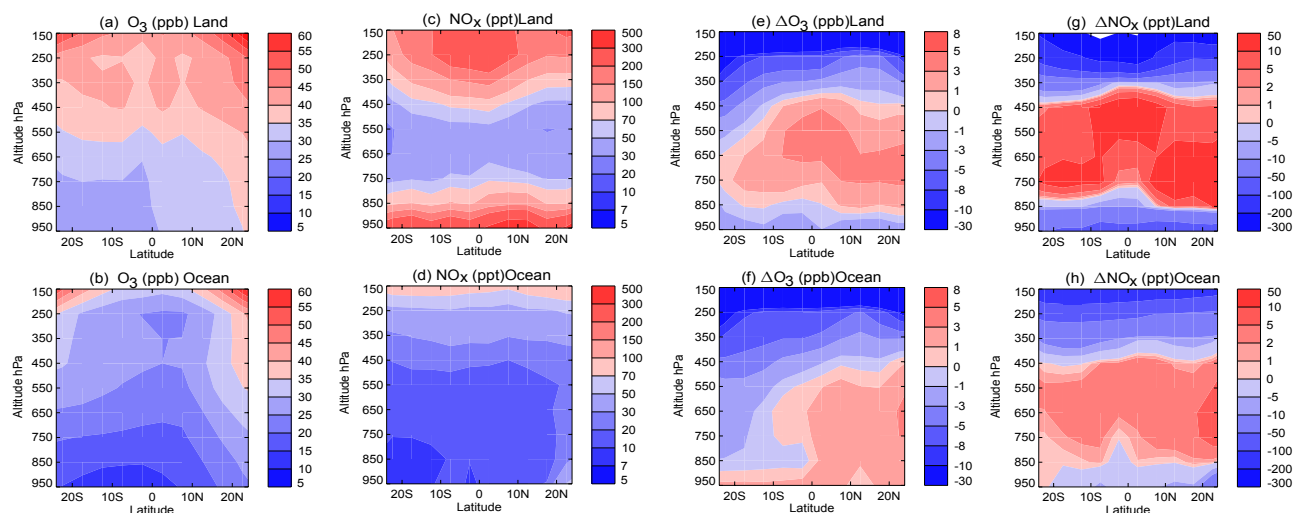


Fig. 3. 20-year average tropical land and ocean O_3 (ppb) (a, b) and NO_x (ppt) (c, d) for the control simulation and O_3 (e, f) and NO_x (g, h) differences control – convection off simulations.

O_3 – produce the O_3 gradient from the surface (25–35 ppb over land, 10–25 ppb over oceans) to the UT (40–60 ppb over land, 30–55 ppb over oceans) (Figs. 3a–b). There are comparable NO_x mixing ratios in the LT and UT over land (“C”-shaped profile – Fig. 3c; above 100 ppt in the LT and UT). Over the oceans UT NO_x is also high (Fig. 3d). Based on the large land/ocean lightning ratio we assume that high values of UT NO_x over the oceans arises from advection of UT land lightning NO_x emissions (with a small contribution from lightning over the oceans, Sect. 2).

Both land and ocean regions show large decreases in UT O_3 (10–30 ppb) and NO_x (up to 100–300 ppt over land; 50–200 ppt over the ocean) due to convection (Figs. 3e–h). LT O_3 and NO_x also decrease over land regions (1–3 ppb and 10–100 ppt, respectively, Figs. 3e, g), but show divergent behaviour over the ocean, where O_3 increases slightly (0–3 ppb), whilst NO_x decreases slightly (5–10 ppt) (Figs. 3f, h). Conversely, MT O_3 and NO_x generally increase over land (by 0–5 ppb and 2–50 ppt, Figs. 3e, g), and over the oceans north of 10° S. Over the remote oceans, south of 10° S, MT O_3 decreases (0–5 ppb) and MT NO_x increases slightly (0–5 ppt) (Figs. 3f, h).

Figure 4 displays vertical changes in tropical O_3 chemical production and destruction when convective mixing is switched on. Since NO is the main species involved in O_3 production, the changes in O_3 chemical production with convective mixing are generally similar to that of NO_x changes (compare Figs. 4a–b, 3g–h). However there are some differences. In particular, UT O_3 production increases over land, whereas NO_x decreases, and surface decreases are large. O_3 chemical destruction is primarily determined by water vapour concentrations and the O_3 vertical distribution (mainly through the $\text{H}_2\text{O}+\text{O}(^1\text{D})$ reaction). As water vapour concentrations do not change between experiments (Sect. 2),

the changes in O_3 chemical destruction are similar to the changes in O_3 (compare Figs. 4c–d, 3e–f), although again there are some differences. Net O_3 chemical production increases in the MT and UT, and decreases at the surface over land (Fig. 4e). Over the oceans, net O_3 production decreases at the surface and in the UT, and in the MT increases over remote regions but decreases elsewhere (Fig. 4f).

The effects of convection on NO_x can partly be understood in terms of a flattening of the tropical land “C”-shaped profile (Fig. 2a), and we assume advection of this effect of over the oceans (Figs. 2a, b, 3a, b). This partly occurs in our model as UT NO_x from lightning emissions is displaced to lower altitudes, and surface NO_x emissions are lifted to higher altitudes, which results in higher NO_x concentrations in the MT (Figs. 3g–h). However, the UT NO_x decreases over land are larger than NO_x increases in the MT by an order of magnitude, suggesting that mixing of NO_x is not the only factor influencing NO_x concentrations (Figs. 3g–h). As discussed in Sect. 1, convection also affects non-methane hydrocarbons (NMHCs) including isoprene, lifting these gases and their degradation products into the UT (Collins et al., 1999). Isoprene has a very short lifetime ($<1\text{h}$; Seinfeld and Pandis, 1997), and is emitted in substantial quantities from tropical vegetation (Guenther et al., 1995; Sanderson et al., 2003b). The natural source of isoprene is much larger than the mainly anthropogenic sources of other NMHCs in the tropics. Here, the prevalence of isoprene, together with its short lifetime, means that its distribution is strongly affected by convection. Figure 5a shows that convection increases MT and UT isoprene at the expense of surface; these changes are largest over equatorial land. Convective lifting of isoprene brings the peroxy acetyl radical (CH_3COO_2), an isoprene degradation product, into contact with lightning NO_x . This leads to significant PAN formation in the cold UT over equatorial land

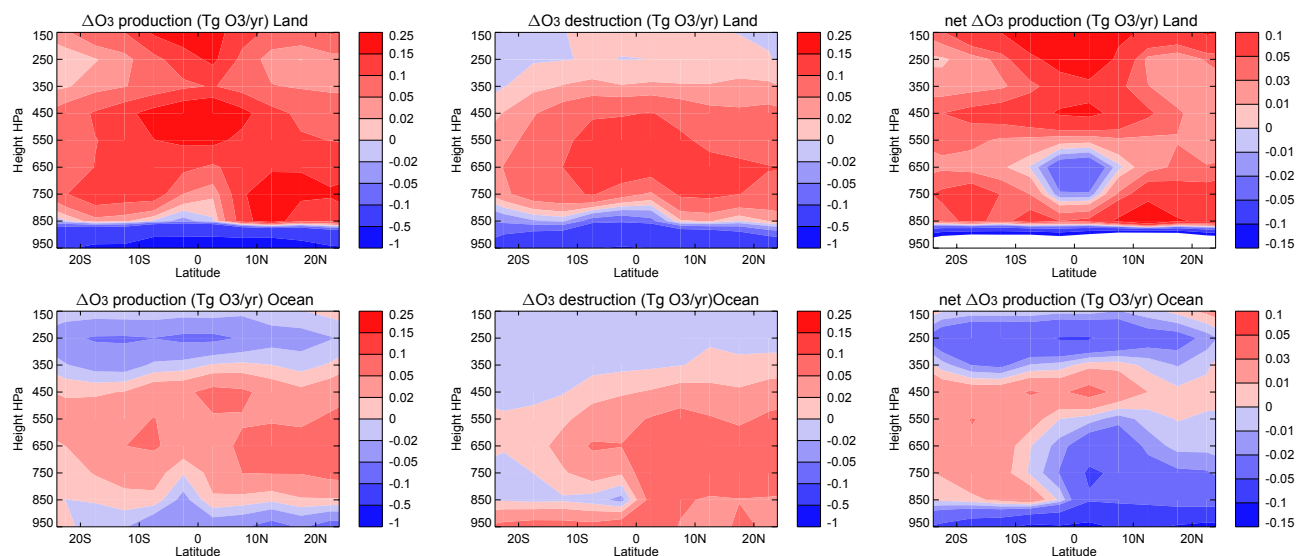


Fig. 4. 20-year average tropical land and ocean O₃ production (a, b), O₃ destruction (c, d) and net O₃ chemical production (e, f) (Tg O₃) control-convection off simulations.

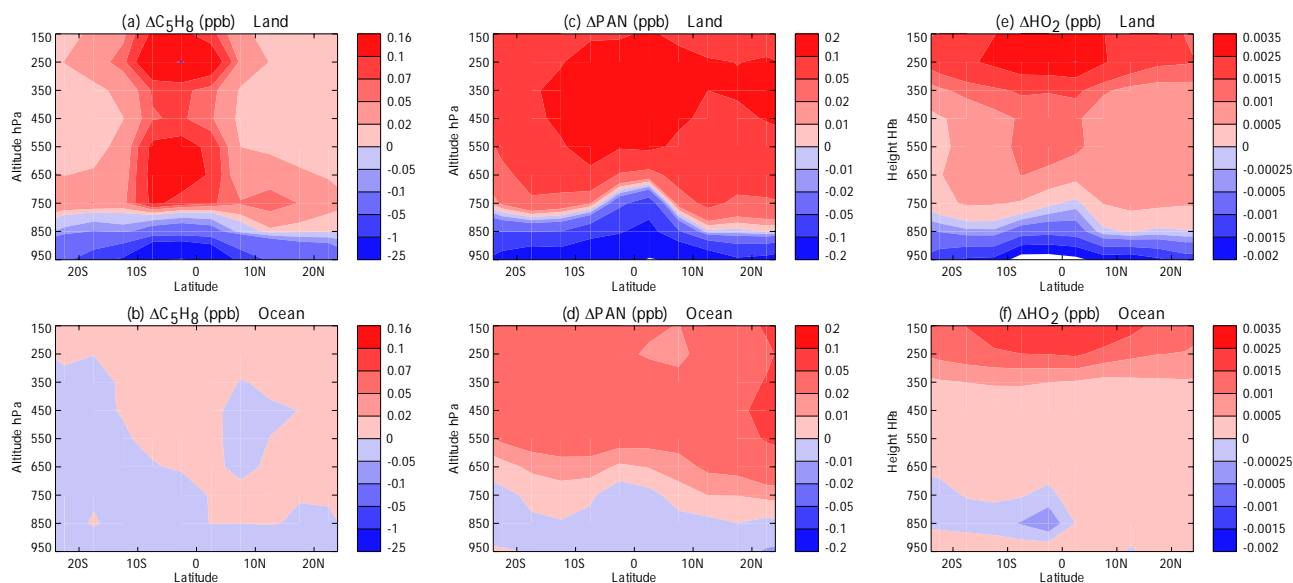


Fig. 5. 20-year average tropical land and ocean isoprene (a, b), PAN (c, d) and HO₂ (e, f) differences (ppb) control-convection off simulations.

at the expense of NO_x (Figs. 5c, 3g). We suspect the higher UT PAN and lower UT NO_x concentrations over the oceans result from these changes over land (Fig. 5d). In parallel sensitivity experiments with no lightning NO_x emissions we find that the impact of convective mixing, in terms of tropical PAN increases, is reduced by ~50%. This indicates that convected isoprene is a significant source of PAN in the UT. PAN acts as a reservoir for NO_x, and its breakdown to release stored NO_x is strongly temperature dependent – in the cold UT PAN is relatively stable and has a lifetime of the or-

der of months. Comparing changes in NO_x and PAN in the UT (350–150 hPa) we find UT NO_x decreases by 0.032 Tg N (50% decrease) and a UT PAN increases by 0.028 Tg N (65% increase). In terms of N conservation we therefore expect that a substantial fraction of the NO_x decrease arises from the PAN increase. Thus the impact of convection on NO_x is through convective transport of NO_x itself in combination with isoprene-PAN-NO_x chemistry in the UT.

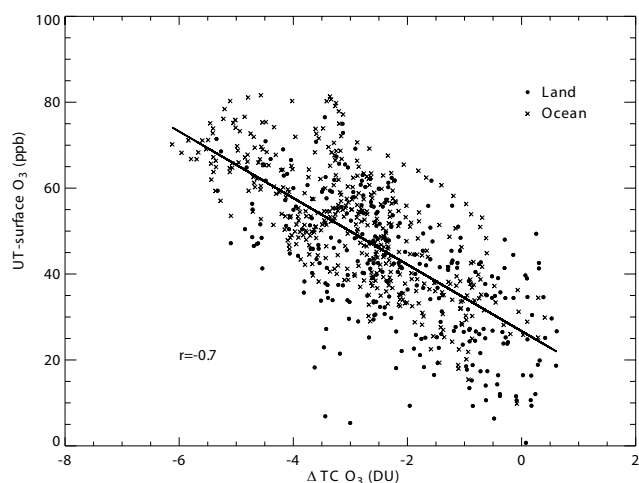


Fig. 6. 20-year annual-average change in TTC O₃ (DU) (control-convection off) vs. UT (350–150 hPa) – surface (950 hPa) O₃ (ppb) (convection off experiment) for combined tropical land and ocean grid boxes.

For O₃, as discussed above for NO_x, upward transport of LT air over land and ocean displaces UT O₃-rich air, which subsides downwards. Over land, similar to NO_x, convection moves O₃ away from its source regions, raising MT concentrations. Therefore vertical mixing of the O₃ profile itself, as well as changes in the NO_x distribution, cause the changes in the O₃ distribution over polluted land. However, changes in UT NO_x over land contrast with changes in UT O₃ production over land. Despite a large reduction in UT NO_x (Fig. 3g) with convective mixing, UT O₃ production increases (Fig. 4a). The role of isoprene is again important here, as its oxidation generates peroxy radicals (HO₂ and RO₂), which are required for O₃ production. O₃ production in the tropical UT tends to fall due to the reduction in UT NO_x, but this effect is more than offset by an increase in UT HO₂ produced from isoprene (Figs. 5e, f). As HO₂ also destroys O₃, the HO₂ increases explain the small equatorial land UT O₃ destruction increases (Fig. 4c). Despite an overall increase in net chemical production in the UT, O₃ decreases. This indicates that vertical transport of O₃ itself is more important than changes in chemistry in determining the outcome of convective mixing in the UT. Over the remote southern oceans, MT O₃ decreases and surface O₃ increases in contrast to NO_x and O₃ production changes. This also implies that over remote tropical locations vertical transport of O₃ itself is more important than changes in NO_x chemistry.

To summarise, convection therefore influences modelled O₃ distributions by a combination of vertical transport of O₃, as well as by affecting the vertical distribution of its precursors, especially NO_x and HO₂ and the resultant chemical production and destruction of O₃. Vertical transport appears to be the dominant process in clean air, over the remote oceans in the MT and LT, and in polluted land regions in the UT.

Elsewhere both convective transport and chemistry changes contribute significantly to the overall impact of convection on the O₃ distribution. The impact of convective mixing is summarized in Table 2.

To assess the influence of vertical transport on the O₃ distribution the relationship between the O₃ gradient in the convection off experiment and the change in TTC O₃ due to convection was examined for all grid boxes over the tropics (Fig. 6). A strong correlation was found ($r=0.7$). For each 10 ppb steepening in the O₃ gradient between the UT (350–150 hPa) and surface (950 hPa), convection reduces TTC O₃ by 1.5 DU (Fig. 6). The relationship is stronger if the change in UT O₃ alone is considered ($r=0.9$, not shown). This also suggests that vertical transport of O₃ plays a major role in the resultant O₃ distribution after convection, particularly in the UT.

3.3 Influence of convection in the extra-tropics

Deep convective mixing has a global effect on O₃ distributions (Fig. 7a). UT O₃ not only decreases in the tropics but also decreases by similar amounts in the mid-latitudes and polar regions (10–30 ppb).

Over the northern mid-latitudes (Fig. 1) some deep convection reaches the UT, especially over parts of the North American and Asian continents. Examination of the large-scale flow in HadAM3 suggests that the large tropical anomalies may also be transported latitudinally, and downward along the subtropical front in the northern mid-latitudes. Consequently, both latitudinal transport and convective mixing in the northern mid-latitudes are likely to contribute to the simulated UT O₃ decreases. In the southern mid-latitudes, some deep convection also occurs over the southern oceans (Fig. 1). We suspect this is the main cause of UT O₃ decreases in the southern hemisphere.

The slightly lower O₃ stratospheric influx when convective mixing is switched on (Table 1) may also contribute to lower extra-tropical UT O₃. Convective mixing also influences NO_x distributions well outside the tropics (Fig. 7b). The changes are highly skewed towards the Northern Hemisphere reflecting the large surface NO_x emissions in this region. Tropical UT NO_x decreases (100–200 ppt) are transported latitudinally, which together with mid-latitude convection results in negative UT NO_x anomalies extending to 45° in the Northern Hemisphere.

In northern mid-latitudes, convection generally reduces surface O₃ and NO_x (except for O₃ around 60° N), which reflects enhanced venting of polluted continental NO_x and O₃-rich air by shallow convection (Figs. 7a, b). The increase of O₃ accompanied by a large decrease of NO_x (100–200 ppt) around 60° N is the titration effect which occurs over North-Western Europe. This effect occurs under very high NO_x levels predominantly in winter (when there are low UV levels for NO₂ photolysis) whereby NO reacts with O₃ to form NO₂. Thus with convective mixing, surface air low in O₃

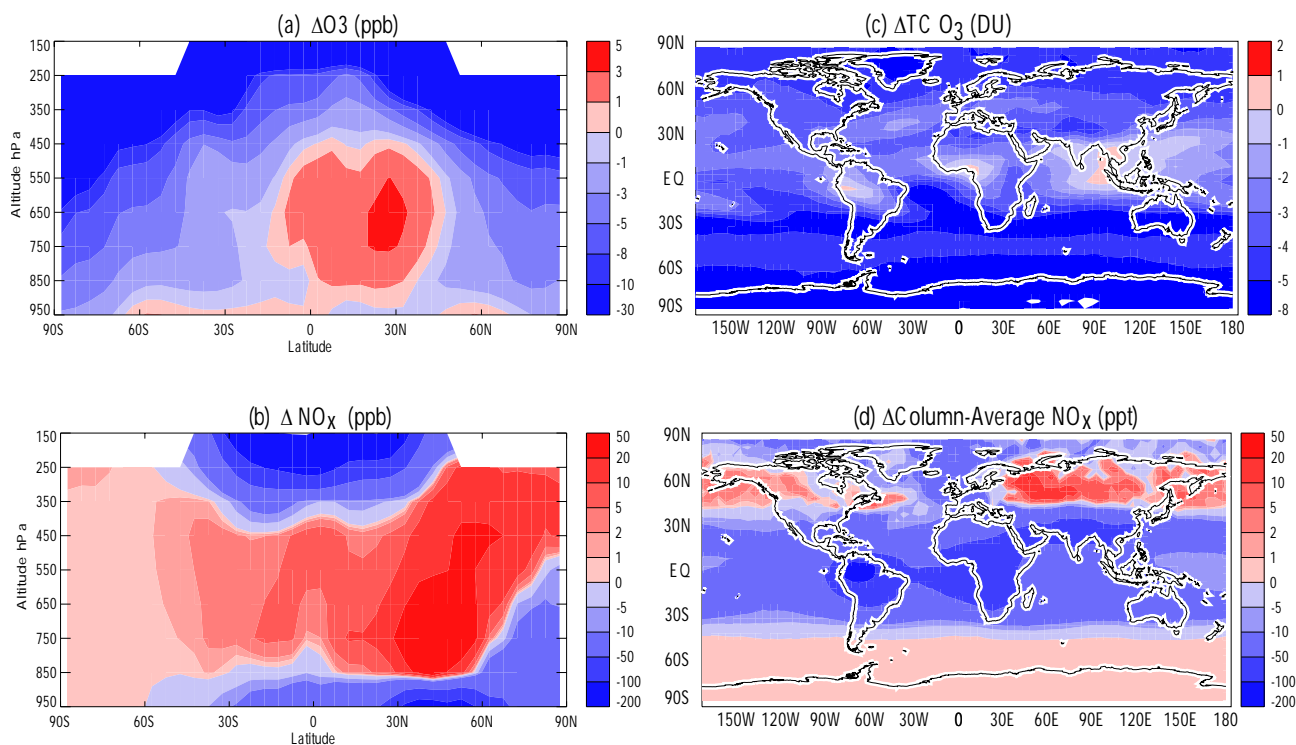


Fig. 7. 20-year average global change in O₃ (ppb) (a) NO_x (ppt) (b) TC O₃ (DU) (c) and column-average NO_x (ppt) (d) for control – convection off simulations.

and high in NO_x is replaced by air with higher O₃ and lower NO_x concentrations. In the polar regions, large-scale subsidence of UT air, that is less rich in O₃ due to hemispheric transport, results in lower surface O₃. At northern polar latitudes LT NO_x levels are highest during winter months and the impact of convective mixing is largest. Shallow convection that lifts NO_x upwards from the LT and MT, combined with transport of the mid-latitudinal anomaly generates negative LT/MT NO_x anomalies over the Arctic (Fig. 7b). In the southern mid-latitudes as in the southern tropics, where precursor emissions are lesser, surface O₃ increases and NO_x decreases slightly.

MT O₃ increases in the northern mid-latitudes up to around 40° N, as in the northern tropics, but decreases elsewhere in the mid-latitudes and polar regions. We suspect that large scale subsidence of large UT anomalies dominates the vertical O₃ distribution (Fig. 7a). Convection produces strong MT NO_x increases (10–50 ppt) in the northern mid-latitudes at the expense of the surface (Fig. 7b). These mid-latitudinal MT NO_x increases appear to be transported to the remote troposphere.

In the column average, convective overturning leads to tropospheric column (TC) O₃ decreases almost everywhere (Fig. 7c). Decreases are largest (up to 8 DU) over the clean southern ocean regions where surface O₃ concentrations are lowest and therefore the effects of deep convection that reaches the UT are presumably greatest. Over equato-

rial land regions, where MT O₃ increases are greatest, TC O₃ decreases are smallest (0–2 DU) and in small areas above strong NO_x source regions (e.g., SE Asia) TC O₃ increases slightly (0–1 DU). Tropospheric column-average NO_x also decreases (strongly) over tropical land regions (50–100 ppt, Fig. 7d) and outflow oceanic regions. The northern mid-latitudes show increases over land and Pacific regions with the largest changes (10–50 pptv, Fig. 7d) over western Eurasia, reflecting upward mixing in convective regions.

As over tropical land, chemical O₃ production increases in the northern mid-latitudes in the MT and UT and decreases strongly at the surface over both land and ocean to ~45° N, reflecting NO_x changes (not shown). O₃ chemical destruction exhibits similar behaviour as in the tropics (not shown). It decreases at the surface over land and increases over oceans, and increases in the MT; UT changes are small. These changes weaken with higher latitude, reflecting the O₃ distribution changes. Overall net chemical O₃ production increases in the MT and UT, with the largest changes between 30°–45° N, where there is some O₃ chemical production, but little destruction. Table 2 provides a summary of the impact of convective mixing over polluted regions between 30° S–45° N and remote oceanic regions.

Table 1. 20-year average O₃ budget changes (control – convection off).

| Budget term Tg (O ₃)/yr | 20-year average control Mask=O ₃ >150 ppb | 20-year average convection off Mask=O ₃ >150 ppb | % change with convective mixing Mask=O ₃ >150 ppb | 20-year average control Mask=PT | 20-year average convection off Mask=PT | % change with convective mixing Mask=PT | Lawrence et al. (2003) % change | Lelieveld and Crutzen (1994) % change |
|--|--|---|--|---------------------------------------|--|---|---------------------------------------|---|
| O ₃ chemical production | 4712 (86) | 4547 (108) | +3.6 | 4709 (87) | 4541 (108) | +3.7 | +16.7 | +14 |
| O ₃ chemical destruction | 4224 (84) | 4097 (102) | +3.0 | 4223 (84) | 4096 (103) | +3.0 | +15.0 | +22 |
| O ₃ net chemical production | 489 (15) | 450 (21) | +8.6 | 487 (15) | 446 (21) | +9.1 | +81.8 | –25 |
| O ₃ dry deposition | 881 (7) | 851 (13) | +3.5 | 881 (7) | 851 (13) | +3.5 | +7.0 | +15 |
| O ₃ stratospheric influx | 392* (15) | 401* (21) | –2.2 | 395* (15) | 405* (21) | –2.6 | –2.1 | |
| O ₃ burden (Tg O ₃) | 250 (3) | 289 (6) | –13.8 | 243 (3) | 281 (6) | –13.4 | +11.9 | –20 |
| O ₃ lifetime (days) | 17.8 (0.2) | 21.2 (0.4) | –16.2 | 17.3 (0.2) | 20.7 (0.4) | –15.8 | –2.5 | |
| NO _x burden (Tg N) | 0.153 (0.002) | 0.194 (0.006) | –27.5 | 0.151 (0.002) | 0.192 (0.006) | –21.2 | +14 | –30 |
| NO _x lifetime (days) | 1.1 ⁺ | 1.4 ⁺ | –21.6 | | | | | |
| PAN burden (Tg N) | 0.320 (0.006) | 0.264 (0.007) | +21.2 | 0.319 (0.006) | 0.263 (0.007) | +21.4 | | |
| OH burden (Tg OH) | 203 (4) | 187 (3) | +8.3 | 201 (4) | 186 (3) | +8.5 | | |

* not significantly different at the 0.01 level.

⁺ This is the NO_x lifetime change for the entire model domain-surface up to 100 hPa. We do not archive sufficient 3-D fluxes to be able to calculate the NO_x lifetime using a tropopause mask.

O₃ chemical production reactions are: NO+HO₂, NO+CH₃O₂, NO+RO₂.

O₃ chemical destruction reactions are: O¹D+H₂O, O₃+OH, O₃+HO₂, O₃+hydrocarbons (C₂H₄, C₃H₆(2 routes), C₅H₈, Methyl vinyl ketone) and other minor net O₃ losses.

3.4 Influence of convection on the global tropospheric O₃ budget

Global tropospheric budgets for O₃ with and without convective mixing are calculated in Table 1.

The global budgets have been calculated using two different masking techniques in order to assess uncertainty arising from use of the 150 ppb isopleth to determine the tropopause. The first 3 columns in Table 1 show results using the 150 ppb tropopause definition, and the next three columns show results using the HadAM3 physical tropopause. As discussed in Sect. 2, the same mask is used in the control and convection off simulations. The 20-year annual-average budget terms are calculated to be similar for the two tropopause definitions, thus the values given below are based on the physical tropopause definition. Annual-average standard deviations are also tabulated. Larger interannual variability occurs in the convection off simulation. This is presumably due to steeper concentration gradients through the troposphere in the absence of convective mixing.

Chemical production increases globally by 3.7%, mainly due to tropical and northern mid-latitude MT NO_x increases (Figs. 7b, 4a). Global chemical destruction also increases (by 3.0%) as a result of MT O₃ increases (Figs. 7a, 4c). Because net chemical production is the small residual of two large budget terms it has a relatively large increase of 9.1%. Dry deposition (which increases with surface O₃) globally increases by 3.5%. All annual-average O₃ fluxes are significantly different (at the 0.01 level) between the control and convection off simulations, bar stratospheric input (Table 1). Despite increased global net chemical production due to tropical MT increases, the global O₃ burden decreases by 13.4%. Likewise, the O₃ lifetime decreases globally from

20.7 to 17.3 days (15.8%). The global NO_x burden also decreases globally by 21.2% and PAN increases by a similar amount. We estimate that the NO_x lifetime decreases by ~20% with convective mixing; mainly due to the downward transport of lightning NO_x emissions (since there are lightning NO_x emissions in the convection off case). The OH burden increases by 8.5% as a result of greater O₃ destruction (and hence OH production) with convective mixing. The differences in burdens between the control and convection off experiments are significant at the 0.01 level for all species mentioned above.

4 Discussion

Lelieveld and Crutzen (1994) calculated a 20% decrease in the global O₃ burden due to convective mixing, using a global model with no NMHC chemistry. In their model, they found that the effects of mixing O₃ over-rode any chemical effects due to mixing of O₃ precursors. More recently, Lawrence et al. (2003), using a global model with detailed NMHC chemistry (similar to that used in this study), found a global O₃ burden increase of 12% from convective mixing. In their study, Lawrence et al. (2003) found the effects of changes in precursor chemistry due to mixing (in particular lifting of surface NO_x emissions) to outweigh the effect of vertical mixing of O₃ itself. In our study with the STOCHEM-HadAM3 model, O₃ decreases by 13% due to convective mixing, and the effect of O₃ vertical transport outweighs the effect of precursor mixing changes (Table 1; Fig. 7a). Differences in the patterns of TC O₃ change are large with decreases almost everywhere in our study, compared to increases everywhere in Lawrence et al. (2003).

Table 2. Summary of the impact of convective mixing on polluted and remote regions. The largest impact is in bold print.

| Process | Impact on O ₃ over polluted land (45° N–15° S) | Impact on O ₃ over remote oceans (0°–60° S) | Dominant impact |
|---|---|---|---|
| Convective transport of O ₃ | UT O ₃ ↓ MT O ₃ ↑ Surface O ₃ ↓ | UT O ₃ ↓ MT O ₃ ↓ Surface O ₃ ↑ | Overall TCO decreases except in parts of SE Asia |
| Convective transport of NO _x n.b. lightning emissions in both simulations | UT NO _x ↓ MT NO _x ↑ Surface NO _x ↓ | UT NO _x ↓ MT NO _x ↑ Surface NO _x ↓ | Largest changes over polluted regions and in the UT UT O ₃ Production ↓ MT O ₃ Production ↑ – (largest changes 30°–60° N) Surface O ₃ Production ↓ – (largest changes 30°–60° N) |
| Convected C ₅ H ₈ ⇒ HO ₂ +RO ₂ | UT O ₃ Production ↑ UT O ₃ destruction ↑ | | UT Net O ₃ production ↑ |
| Convected C ₅ H ₈ ⇒ NO _x to PAN conversion | UT NO _x ↓ | | UT O ₃ Production ↓ |

One similarity between the Lawrence et al. (2003) and this study is that MT O₃ increases due to mixing of precursor NO_x emissions. Lawrence et al. (2003) also report O₃ budgets for their simulations. In common with this study, they find that switching on convection results in an increase in production of O₃, although they find a larger percentage increase (Table 1). Another similarity is that convection reduces the tropospheric O₃ lifetime. The impact of convective mixing on tropospheric O₃ lifetime is much stronger in our study. As discussed in Sect. 3.1, of all the models sampled in a recent intercomparison (Stevenson et al., 2005b), STOCHEM-HadAM3 had the shortest lifetime (17 days), whereas MATCH-MPIC had the longest (28 days). We might therefore expect some significant differences in the responses of these two models to convection, even if the convective mass fluxes were quite similar. With the larger reduction in tropospheric O₃ lifetime, the tropospheric O₃ burden falls in our study, whereas Lawrence et al. find an increase. The reduction in lifetime in our results arises mainly due to a reduction in UT O₃ concentrations. In our model these UT O₃ reductions are driven mainly by the vertical mixing of O₃, as we find they occur despite increases in land UT chemical production (Fig. 4a). An interesting observation is that land UT chemical production increases despite large reductions in NO_x (Figs. 4a, 3g) – this indicates that HO_x increases (Figs. 5e, f) outweigh the NO_x decreases (Figs. 3g, h). In the Lawrence et al. (2003) study UT O₃ increases, which suggests that UT O₃ production increases are greater than in our study.

Do the differences in the impact of convective mixing in these two contemporary models represent a realistic uncer-

tainty range? To answer this question we need to understand the root causes of these inter-model differences. Below we investigate potential model differences.

In both studies, the water vapour distribution and lightning NO_x emissions were kept constant between the control and convection off (or equivalent) simulations.

Differences in the convection schemes themselves (Prather et al., 2001) may be an important, if not the most important cause, of the different effects of convective mixing on the O₃ burden in the two studies. In particular, differences in the height and strength of convection (Olivie et al., 2004) and efficiency of vertical transport of NO_x and O₃ out of the boundary layer (Beekman et al., 2003) may be crucial. Annual-average convective updraught mass fluxes simulated in HadAM3 and MATCH-MPIC (Rasch et al., 1997) models are displayed in Fig. 1 for years 1991–1996 and 1995, respectively. Annual-average convective mass fluxes for 1991–1996 and the year 1995 are similar in HadAM3, showing 1995 to be a typical year within the 1991–1996 period.

The strength of convective updraught fluxes in the tropics and mid-latitudes is typically a factor of 2–3 stronger everywhere in HadAM3 compared to MATCH-MPIC (Figs. 1a–c, g–i). Whilst HadAM3 has generally stronger and higher convection compared to ERA-40- (Figs. 1a–f), MATCH-MPIC shows weaker and less deep convection (Figs. 1g–i). In particular, there is much less convection in the upper UT in MATCH-MPIC. This implies more vigorous and extensive deep convection in the HadAM3 model. There is general agreement between the two models in the location of convective updraughts in the MT (Figs. 1b, h), except that there is little convection over the Eastern Pacific branch of

the ITCZ in MATCH-MPIC. In the UT (Figs. 1a, g) there are much greater differences between the simulated convective updraught fluxes. In particular, HadAM3 exhibits much greater convection across the ITCZ, and shows greater deep convection in mid-latitude regions.

Olivié et al. (2004) compared the impact of using convective mass fluxes derived from two different methods on tropospheric O₃ distribution. One source of convective mass fluxes was directly archived “on-line” ERA-40 reanalyses, the other a convective parametrisation in the TM3 model based on large-scale wind, temperature, evaporation and humidity fields from ERA-40 reanalyses. In this case convective mass fluxes are derived “off-line”. Both derived mass fluxes are based on Tiedtke (1989), but have different modifications to their underlying schemes. The datasets also have different temporal averaging properties (time-averaged vs. instantaneous). One of the main differences reported by Olivié et al. (2004) was that convective mass fluxes reach higher altitudes in the ERA-40 on-line reanalyses compared to those diagnosed off-line. Comparing the results from simulations performed using their on-line and off-line convection schemes Olivié et al. (2004) find lower O₃ and NO_x concentrations in the UT and higher concentrations in the free troposphere as a result of the deeper convection in the ERA-40 on-line scheme. This promoted greater transport of O₃-poor air from the surface to the UT, as well as more subsidence to the MT. Therefore, we expect that it is the higher and larger amount of convection that leads to the substantial reduction of tropical UT O₃ in STOCHEM, which is not seen in the MATCH-MPIC simulations. Olivié et al. (2004) also report a reduction in tropical UT O₃ concentrations using on-line compared to off-line ERA-40 reanalyses convective mass fluxes. They suggest that these tropical anomalies are transported to higher latitudes through latitudinal transport, and transport downward along the subtropical front. The lower O₃ concentrations with greater and higher mixing in the UT, is in agreement with the patterns of change in the sub-tropics displayed in Fig. 7a. In the mid-latitudes, Olivié et al. (2004) find larger O₃ concentrations in the MT with larger/higher convection in the simulations that use the fluxes from the ERA-40 reanalyses. These arise from enhanced downward transport in the higher latitudes. However, despite greater and higher convection in the mid-latitudes in STOCHEM-HadAM3 relative to MATCH-MPIC (Figs. 1b, h), MT increases are smaller. Therefore, we suspect differences other than those arising from the convection schemes also contribute to the contrasting effects of convective mixing displayed by the STOCHEM and MATCH-MPIC models. Interestingly, the relative effects of convection on O₃ budget fluxes are larger in the MATCH model compared to STOCHEM, despite the generally smaller convective mass fluxes; this may be related to the longer tropospheric O₃ lifetime in MATCH-MPIC (Table 1).

Differences in chemistry potentially arise from differences in both emission source strengths and chemical schemes.

A comparison of the emissions used in the two studies shows that NO surface, aircraft and ship emissions are similar but lightning NO_x emissions are higher at 7 Tg N/yr in our study compared to 2 Tg N/yr in Lawrence et al. (2003) (M. Lawrence, personal communication); anthropogenic NMHC emissions are also higher by 5–20 Tg/yr in STOCHEM, and isoprene is higher by ~225 Tg/yr (~65%) compared to MATCH (von Kuhlmann et al., 2003). The higher isoprene and lightning NO_x emissions in our study may result in greater amounts of PAN formation and consequently a larger UT NO_x reduction, although higher isoprene also suggests higher UT HO_x. Emissions of both lightning NO_x and isoprene from vegetation carry high levels of uncertainty, and it is unclear whether the higher or lower levels of emissions more closely resemble the real world. Both these natural sources are sensitive to climate, and thus likely to respond to changes in climate (Stevenson et al., 2005a).

In addition, there may be significant model differences in chemical schemes in the two studies, particularly in the isoprene degradation schemes. The isoprene-lightning NO_x interaction may be much less important in the MATCH model, resulting in larger increases in O₃ production with convection. In STOCHEM, this mechanism limits the effectiveness of convection in promoting chemical production of UT O₃, and consequently the impact of vertical O₃ mixing is the process of overriding importance. Figure 2 shows simulated tropical PAN to be in agreement with observations to within ± 1 standard deviation. There is some overestimation of PAN in parts of the UT, but also some overestimation of UT NO_x (Sect. 3.1). Therefore, promotion of the conversion of NO_x into PAN by convection seems a plausible process, since it acts to bring simulated NO_x concentrations into better agreement with observations. However, other mechanisms such as excessive lightning NO_x emissions or errors in their vertical distribution could also explain the UT NO_x overestimates in the tropics. In a model sensitivity study, von Kuhlmann et al. (2004) found that both isoprene and lightning emissions magnitudes, and isoprene degradation schemes, all had important influences on tropical O₃. Further model sensitivity studies are needed to clarify how different emissions and isoprene schemes influence tropospheric O₃ response to convective mixing.

Finally, vertical resolution and upper boundary conditions for O₃, as discussed by Lawrence et al. (2003) could be another source of different responses with convective mixing. However, although the vertical grid resolution is lower in STOCHEM than in the MATCH-MPIC model used in the Lawrence et al. (2003) study the Lagrangian sampling in STOCHEM is at roughly the same resolution (50 000 air parcels compared to $64 \times 32 \times (\sim 20$ tropospheric vertical levels) = approximately 41 000 grid cells in the troposphere).

5 Conclusions

Model experiments have been performed to examine the role of deep convective mixing in determining the distributions of tropospheric O₃ and its precursors. In contrast to results from an earlier study with a model of similar chemical complexity (Lawrence et al., 2003), convective mixing in our study reduces the O₃ burden, due to vertical O₃ redistribution and associated lifetime changes. Convection of O₃ precursors has several competing effects on O₃ chemical production. Over tropical land, convection lofts surface sources of NO_x and NMHCs in particular isoprene, tending to increase their concentrations in the MT and UT at the expense of the LT. However, in our model the subsidence associated with convection mixes downwards UT lightning NO_x. UT NO_x is also converted to PAN by the introduction of peroxy acetyl radicals, an oxidation product of isoprene. The overall effect is a reduction in UT NO_x, together with an increase in UT HO_x; the net effect is a small increase in O₃ production. However, this increase in O₃ production is more than counteracted by the effects of convective mixing of O₃ itself, and UT O₃ reduces. The features generated over the tropical land are assumed to be advected over the tropical oceans, although over the remote oceans, the impact of local vertical mixing becomes more dominant. Mid-latitude convection also reduces UT O₃ resulting in a 13% decrease in the global O₃ burden despite a 4% increase in chemical production. This apparent contradiction arises because the mean tropospheric O₃ lifetime reduces substantially (by 16%); this is mainly because less O₃ resides in the UT, where its lifetime is longest. Comparison of convective mass fluxes from this study and that of Lawrence et al. (2003) reveal substantial differences in the strength and height of deep convection. We suspect that differences in isoprene chemistry schemes as well as lightning NO_x and isoprene emissions magnitudes are also important. With such divergent results from two apparently similar models (in terms of resolution and complexity), and the importance of deep convective mixing processes in altering the state of the atmosphere on interannual and longer timescales, further studies with other models are needed to constrain this range of uncertainty.

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